

5-11-62

(51) International patent classification 5: [numbers]	A1	(11) International publication No.: WO 92/16183 (43) International publication date: 1. October 1992
(21) International reference No.: (22) International application date (30) Priority dates: (71) Applicant <i>(for all target countries except US)</i> : (72) Inventor; and (75) Inventor/Applicant <i>(for US only)</i> : (74) Attorneys:		(81) Target countries:  <i>Published with international search report.</i>

(54) Title: USE OF COMPOSITIONS BASED ON ORGANICALLY MODIFIED POLYCONDENSATES OF SILICIC ACID FOR COATING TEETH AND TOOTH REPLACEMENT PARTS.

(57) Abstract

Compositions for coating teeth and tooth replacement parts are made from at least one compound of formula  $MR_x$  which is soluble in the reaction medium, wherein M stands for Ti, Zr, Si, Ge, Sn or Al, R stands for halogen, hydroxy, alkoxy, acyloxy or a chelate ligand and x is the valency of M, b) an organic silane of formula  $R''_nSiX_{4-n}$ , wherein R'' stands for alkyl, alkenyl, aryl, arylalkyl, alkylaryl, arylalkenyl, alkenylaryl, which residues can be interrupted by oxygen atoms or sulphur atoms or -NH groups, X stands for hydrogen, halogen, hydroxy, alkoxy, acyloxy or the group  $-NR'_2$  (R' = hydrogen and/or alkyl) and n = 1, 2 or 3, and/or c) an organofunctional silane of formula  $Rm''(R''')_nSiX_{(4-m-n)}$ , wherein R'', X and n have the above meanings, R''' stands for alkylene, phenylene, alkylphenylene, or alkenylene, which residues can be interrupted by oxygen atoms or sulphur atoms or -NH groups, Y stands for halogen atoms, hydroxy, mercapto, polyol, e.g. glykyl or glyceryl, possibly substituted amino, quaternary ammonium, amide, polyamide, aldehyde, keto, carboxy, carboxylic acid alkyl ester, sulphonic acid, phosphoric acid, epoxy, acryloxy or methacryloxy groups and m = 1, 2 or 3. The coatings are resistant to deposits of dental plaque.

(57) Abstract  
[in German]

[*country codes*]

Wordcount: 100 [200]  
TD-53A.DOC

---

Use of Compositions Based on Organically Modified  
Polycondensates of Silicic Acid for  
Coating Teeth and Tooth Replacement Parts

---

The invention is concerned with the use of compositions based on organically modified polycondensates of silicic acid for coating teeth and tooth replacement parts.

Teeth and tooth replacement parts, manufactured from a wide range of materials, are subject to the risk of plaque deposit accumulations.

It is the task of the invention to protect teeth and tooth replacement parts against the formation of plaque deposits.

In terms of the invention, this task has been solved by the use of compositions based on organically modified polycondensates of silicic acid. These compositions are applied to teeth or tooth replacement parts and cured. Adhesion is extraordinarily good, an adhesive agent is not required.

Surprisingly, it has turned out that, after their curing, compositions based on organically modified polycondensates of silicic acid form coatings on teeth and tooth replacement parts that are resistant to the formation of plaque deposits. This is especially surprising in view of the fact that, in the German patent 27 58 414, compositions based on organically modified polycondensates of silicic acid are described as coatings of substrates, e.g. glass vessels for growing tissue and cell cultures.

In Column 3, Lines 32ff. of this patent it says that the cells in these conditions – probably due to chemical bonding forces – are firmly attached to this base so that growth of a group of cells is guaranteed. Thus, one would have expected that coatings based on polycondensates of silicic acid would be completely unsuitable for purposes examined in this paper.

The compositions based on organically modified polycondensates of silicic acid, which are to be used in terms of the invention, comprise

- (a) at least one compound soluble in the reaction medium of formula (I)



wherein M stands for Ti, Zr, Si, Ge, Sn or Al, R stands for halogen, hydroxy, alkoxy, acyloxy or a chelate ligand and x is the valency of M, as well as

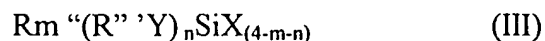
- (b) an organic silane of formula (II)



wherein R'' stands for alkyl, alkenyl, aryl, arylalkyl, alkylaryl, aryl alkenyl, alkenyl aryl, which residues can be interrupted by oxygen atoms or sulphur atoms or –NH groups, X stands for hydrogen, halogen, hydroxy, alkoxy, acyloxy or the group –NR<sub>2</sub>' (R' = hydrogen and/or alkyl) and n has the valency 1, 2 or 3,

and/or

- (c) an organofunctional silane of formula (III)



wherein R'', X and n have the above meanings, R''-Y stands for alkylene, phenylene, alkylene phenylene, or alkenylene, which residues can be interrupted by oxygen atoms or sulphur atoms or -NH groups, Y stands for halogen atoms, hydroxy, mercapto, polyol, e.g. glycol or glyceryl, possibly substituted amino, quaternary ammonium, amide, polyamide, aldehyde, keto, carboxy, carboxylic acid alkyl ester, sulphonic acid, phosphoric acid, epoxy, acryloxy or methacryloxy groups and m has the valency 1, 2 or 3.

These compositions can possibly contain a further component (d):

- (d) low-volatile oxides, soluble in the reaction medium, of an element of the main groups Ia to Va or the secondary groups IVb or Vb of the periodic system, with the exception of titan, zircon, silicon, germanium, tin and aluminum, or, under the reaction conditions, low-volatile oxide forming compounds of one of these elements, soluble in the reaction medium.

Compositions containing the components (a), (b) and (c) as well as possibly (d) are known from the European patent 78548. Its complete, disclosed content should be regarded as part of this paper.

In the above formulae (I), (II) and (III), residues R, R', R'', R'-, X or Y that may occur several times can have the same or different meanings respectively for a compound.

The alkyl residues stand, for example, for straight chained, branched or cyclical residues with 1 to 20, preferably 1 to 10 carbon atoms and in particular lower alkyl residues with 1 to 6, preferably 1 to 4 carbon atoms. Special examples are methyl, ethyl, n-propyl, isopropyl, n-butyl, secondary butyl, tertiary butyl, pentyl, n-hexyl and cyclo-hexyl. The acryl residues contain, for example, 6 to 25, preferably 6 to 14 and in particular 6 to 10 carbon atoms. Special examples are phenyl and naphthyl, where phenyl is preferred.

The alkenyl residues are, for example, straight chained, branched or cyclical residues with 2 to 20, preferably 2 to 10 carbon atoms and in particular lower alkenyl residues such as vinyl, allyl and 2-butenyl.

The alkoxy, acyloxy, alkyl amino, arylalkyl, alkylaryl, aryl alkenyl, alkenyl aryl, alkylene, alkylene phenylene, keto, carboxylic acid alkyl ester and substituted amino residues are derived, for example, from the above-mentioned alkyl, alkenyl, aryl residues. Special examples are methoxy, ethoxy, n- and i-propoxy, secondary and tertiary butoxy, acetyloxy, propionyloxy, monomethyl amino, monoethyl amino, dimethyl amino, diethyl amino, monomethyl anilino, benzyl, tolyl, methylene, ethylene, dimethylene, toluylene and styryl.

The residues mentioned can possibly carry the usual substitutes such as halogen atoms, lower alkyl residues, hydroxy, nitro or amino groups.

Amongst the halogens, fluor, chlorine and bromine are preferred, and chlorine is especially preferred.

Special examples for titanium or zircon compounds of component (a) are  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Ti}(\text{Oi-C}_3\text{H}_7)_4$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Ti}(\text{cresyl})_4$ ,  $\text{Zr}(\text{OC}_3\text{H}_7)_4$ ,  $\text{Zr}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Ti}(\text{acetylacetonato})_2(\text{Oi-C}_3\text{H}_7)_2$ ,  $\text{Zr}(\text{acetylacetonato})_4$  and other titanium or zircon complexes with chelate ligands which are preferably coordinated via oxygen and/or

nitrogen. Special examples for silicon, germanium, tin and aluminum compounds of component (a) are  $\text{Si}(\text{OH})_4$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Si}(\text{OCH}_3)_4$ ,  $\text{Si}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Si}(\text{OC}_3\text{H}_7)_4$ ,  $\text{SiCl}_4$ ,  $\text{GeCl}_4$ ,  $\text{Ge}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Sn}(\text{OC}_2\text{H}_5)_4$ ,  $\text{AlCl}_3$ ,  $\text{Al}(\text{OC}_2\text{H}_5)_3$ ,  $\text{Al}(\text{OC}_3\text{H}_7)_3$ ,  $\text{Al}(\text{OC}_4\text{H}_9)_3$ ,  $\text{Al}(\text{OH})_3$ .

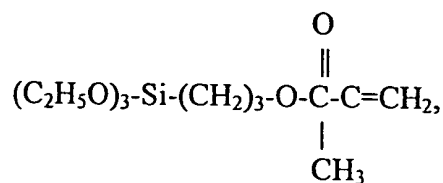
Preferred organic silanes of type (b) are for example:

$(\text{CH}_3)_2\text{-Si-Cl}_2$ ,  $(\text{CH}_3)_2\text{-Si-(OCH}_3)_2$ ,  $(\text{CH}_3)_2\text{-Si-(OC}_2\text{H}_5)_2$ ,  $(\text{C}_6\text{H}_5)_2\text{-Si-Cl}_2$ ,  $(\text{C}_6\text{H}_5)_2\text{-Si-(OC}_2\text{H}_5)_2$ ,  $\text{CH}_2=\text{CH-Si-Cl}_2$ ,  $\text{CH}_2=\text{CH-CH}_2\text{-Si-(OC}_2\text{H}_5)_3$ ,  $\text{CH}_2=\text{CH-CH}_2\text{-Si-(CH}_3\text{COO)}_3$ ,  $(i\text{-C}_3\text{H}_7)_3\text{-Si-OH}$ ,  $(\text{CH}_3)_2\text{-Si-(OH)}_2$  and  $(\text{C}_6\text{H}_5)_2\text{-Si-(OH)}_2$ . Some of these silanes are commercial products or they can be manufactured with known methods; cf. W. Noll, "Chemie und Technologie der Silicone" [*Chemistry and Technology of Silicones*], Verlag Chemie GmbH, Weinheim/Bergstrasse (1968) [*publisher*].

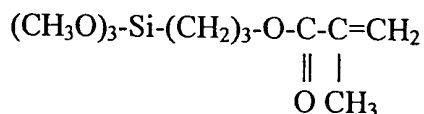
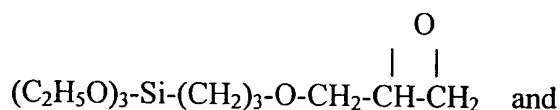
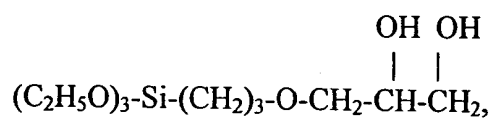
For the organofunctional silanes (c), bridge group R''' can possibly be interrupted by oxygen or sulphur atoms or -NH groups. Preferably, 2 to 10 recurring structural units are formed in this way.

Preferred organofunctional silanes are for example:

$(\text{C}_2\text{H}_5\text{O})_3\text{-Si-(CH}_2)_3\text{-OH}$ ,  $(\text{C}_2\text{H}_5\text{O})_3\text{-Si-CH}_2\text{-NH}_2$ ,  $(\text{CH}_3\text{O})_3\text{-Si-(CH}_2)_2\text{-NH-(CH}_2)_2\text{-NH}_2$ ,  $(\text{C}_2\text{H}_5\text{O})_3\text{-Si-p-C}_6\text{H}_4\text{-NH}_2$ ,  $(\text{C}_2\text{H}_5\text{O})_3\text{-Si-(CH}_2)_3\text{-OH}$ ,  $(\text{CH}_3\text{O})_3\text{-Si-(CH}_2)_4\text{-SH}$ ,  $\text{CH}_3(\text{CH}_3\text{O})_2\text{-Si-CH}_2\text{-CH(CH}_3\text{)-CH}_2\text{-NH-(CH}_2)_2\text{-NH}_2$ ,  $\text{CH}_3(\text{C}_2\text{H}_5\text{O})_2\text{-Si-(CH}_2)_4\text{-NH}_2$ ,  $(\text{CH}_3)_2\text{C}_5\text{H}_5\text{O-Si-CH}_2\text{-NH}_2$ ,  $\text{CH}_3(\text{C}_2\text{H}_5\text{O})_2\text{-Si-CH}_2\text{-OH}$ ,  $(\text{CH}_3\text{-CH}_2\text{-O})_3\text{-Si-CH}_2\text{-CH(CH}_3\text{)-CH}_2\text{-NH-(CH}_2)_2\text{-NH}_2$ ,  $(\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O})_3\text{-Si-(CH}_2)_4\text{-NH}_2$ ,  $(\text{C(CH}_3)_2\text{(C}_2\text{H}_5\text{O)})_3\text{-Si-CH}_2\text{-NH}_2$ ,



[diagram]



For the organic silanes (b) and the organofunctional silanes (c), m preferably has the value 0, and n preferably has the values 1 or 2.

Instead of the monomeric base silanes (b) and (c), pre-condensed oligomers of these silanes, soluble in the reaction medium, can possibly be used; i.e. straight-chained or cyclic, low molecular partial condensates (polyorganosiloxanes) with a condensation degree of e.g. about 2 to 6.

Low-volatile oxides, soluble in the reaction medium, or compounds of elements of the main groups Ia to Va or of the secondary groups IVb or Vb of the periodic system forming such low-volatile oxides are used as component (d). Preferably, component (d)



is derived from the following elements: Li, Na, K, Mg, Ca, B, Pb, P, As and/or V, where Na, Ca, Mg, Sr, B, and P are especially preferred.

Amongst the low-volatile oxides,  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{As}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$  and  $\text{B}_2\text{O}_3$  are especially preferred.

Compounds forming low-volatile oxides soluble in the reaction medium are, for example, inorganic acids such as phosphoric acid and boric acid as well as their esters. Also suitable are, for example, halides such as  $\text{SiCl}_4$  and  $\text{HSiCl}_3$ , and alkoxides such as  $\text{NaOR}$ ,  $\text{KOR}$ ,  $\text{Ca(OR)}_2$  where R is derived from lower alcohols such as methanol, ethanol, propanol or butanol. Further usable base compounds are appropriate salts with volatile acids, e.g. acetates, basic acetates such as basic lead acetate, and formiates.

The compositions comprise 1 to 99, preferably 20 to 90, in particular 40 to 80 mol-% of component (a) and correspondingly 1 to 99, preferably 10 to 80, in particular 40 to 60 mol-% of component (b) or

the compositions comprise 1 to 99, preferably 20 to 90, in particular 40 to 60 mol-% of component (a) and correspondingly 1 to 99, preferably 10 to 80 and in particular 20 to 60 mol-% of component (c) or

the compositions comprise 1 to 98, preferably 20 to 80, in particular 40 to 60 mol-% of component (a), 1 to 98, preferably 10 to 75 and in particular 15 to 50 mol-% of component (b), and 1 to 40, preferably 5 to 30 and in particular 10 to 25 mol-% of component (c).

If component (d) is used, the compositions comprise 0.1 to 50, preferably 0.5 to 30 and in particular 2 to 20 % by weight of component (d), relative to the overall weight of the basic components (a) to (d).

Initially, the preferably water-free basic components are pre-condensed in the desired proportion of materials, possibly with the presence of a water-free, organic solvent and possibly with the presence of a water-free condensation catalyst. Examples of suitable solvents are alcohols, preferably lower alcohols such as methanol, ethanol, or butanol, ether, preferably lower dialkyl ethers such as diethyl ether or dioxan, ketones, e.g. acetone, ester, benzol and their mixtures. The amount of solvent is 0 to 90, preferably 40 to 70 % by weight, relative to the weight of components (a) to (d).

Water-free acids and lyes are used as condensation catalysts for the water-free pre-condensation. Amongst acids available for this purpose are especially the volatile acids such as hydrogen halides or glacial acetic acid, which are possibly dissolved in one of the above-mentioned water-free, organic solvents, or organic acids such as formic acid, acetic acid or propion acid. If alcoholic solutions of volatile acids are used, such as methanolic 1 N HCl, the overall catalyst concentration can, for example, be up to 50 mol-percent; these materials are preferably added as individual portions.

Amongst lyes available for this purpose are inorganic and organic lyes such as ammonium, hydroxide of sodium, potassium or calcium, or tri-alkylamines, where ammonium or tri-alkylamines are especially preferred.

The pre- condensation process is usually carried out at temperatures from  $-20$  to  $200^{\circ}\text{C}$ , preferably from  $50$  to  $150^{\circ}\text{C}$ , and in particular at the boiling temperature of the solvent.

Pre- condensation can also take place in various ways with water present:

1) Partial Hydrolysis:

Addition of under-stoichiometric amounts of water to the component with the slowest reaction. Subsequently, the components more reactive in hydrolysis are added. The addition of water can take place in a more or less gentle way for component (a), for example

- dissolved in alcohol,
- addition of water via a moist atmosphere,
- creation of water in the reaction solution by formation of ester,
- addition of salt hydrates.

2) Addition of compounds that control hydrolysis, e.g. 2,5-pentanedione, acetic acid, acetoacetic acid ester and similar ones,

3) Addition of materials that control drying, such as oxalic acid, formamide and similar ones.

Possibly, one can at first pre-condense part of one, several or all basic components, then mix the remaining basic components and subsequently co-condense hydrolytically or non- hydrolytically.

Generally, pre-condensation is carried out to the extent that the resultant pre-condensate still has a liquid consistency.

The oligomeric or low-molecular, partially hydrolyzed and condensed inorganic-organic pre-condensate can then be isolated and dissolved in an organic solvent to a composition with a defined viscosity. Higher alcohols, esters, e.g. acetic acid ethyl ester or acetic acid amyl ester, toluol, chloroform, acetone and others, are suitable solvents. The viscosity of the coating composition can be set to a value in the range of 5 to 80mPa\*s, which is dependent on the selected coating procedure. The amount of solvent is usually 20 to 95, preferably 40 to 80 % by weight, relative to the weight of the pre-condensate.

Furthermore, auxiliary materials can be added,

such as	Filler materials	0 - 50 % by weight
	Viscosity control agents	0 - 15 % by weight
	Conserving agents	0 - 2 % by weight
	Pigments	0 - 2 % by weight
	Auxiliary process and wetting agents	0 - 5 % by weight
	Stabilizers	0 - 5 % by weight
	Inhibitors	0 - 5 % by weight

(each relative to the overall weight of components (a) to (d)), which allow an individual consistency and color adjustment of the mixtures.

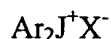
The solutions obtained in this manner are then applied to the dental materials or teeth to be coated, by spraying, immersion or brushing on. The preferred method is either immersion or brushing on. It may be that it is advisable to apply several coats once the solvent has evaporated.

Subsequently, at temperatures between 36° and 120°C, a thermal post-treatment is carried out for just a few minutes up to several hours to reinforce the coating. If organofunctional silanes with ethylenically unsaturated or epoxy-functional groups are present, they can be pre-reinforced via cationic or radical polymerization before further poly-condensation will also occur at room temperature and over a longer time span. In particular it is possible, for the case of functional silanes with ethylenically unsaturated groups, to achieve an initial reinforcement of coatings by radical polymerization, in particular by photo-polymerization. For this purpose, cationic or radical initiators are added to these compositions. Suitable as cationic initiators are for example aryl-diazonium salts, diaryl iodonium salts, triaryl sulphonium salts as well as metallocene[?]-type complex salts. A preferred initiator class for these purposes in terms of the invention are the metallocene[?]-type complex salts, in particular the compound (I):

[diagram]

PF<sub>6</sub> (I)

A further preferred initiator class for cationic polymerization are the diaryl iodonium salts as per formula:



where Ar is a possibly substituted arene[?], e.g. benzol, toluol, xylol, ethyl benzol, methoxy benzol, naphthalene, 1,2-dihydro-naphthalene, phenanthrene, anthrathene, 9,10- dihydro-anthrathene, diphenylene, biphenyl, cumol; and where X<sup>-</sup> is a complex anion, e.g. BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, preferably BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>. Particularly preferred are diphenyliodonium-tetrafluoroborate, ditoluyliodonium-tetrafluoroborate, ditoluyliodonium-hexafluorophosphate and di-t-butylphenyliodonium-tetrafluoroborate. Further suitable diaryl iodonium salts are mentioned in "UV-Curing", Science and Technology, edited by S. Peter Pappas, Technology Marketing Corporation, Norwalk, USA, 06851 (1980).

Examples of suitable formation agents for radicals are organic peroxides, e.g. diacylperoxides such as benzol peroxide and lauroyl peroxide; keto peroxides and cyclohexanon peroxide, hydrocarbon peroxides such as tertiary butylhydro-peroxide, cumolhydro-peroxide and decahydro-naphthalene-hydroperoxide; dihydrocarbon peroxides such as di-tertiary butyl peroxide and dicumyl peroxide; perketals such as 1,1-di-tertiary butylperoxy-3,3,5-trimethylcyclohexan; perester such as tertiary butyl perbenzoate, tertiary butylperoxy-isopropyl percarbonate, tertiary butylperpivalate, tertiary butylperoctoate, tertiary butylcyclohexyl percarbonate and tertiary butylpermaleinate as well as acetylcyclohexansulphonyl peroxide. Also suitable are common azo-initiators such as azobisisobutyro-nitrile.

All photo- initiators known for hardening light-curing synthetics can be considered as photo- initiators. Suitable photo- initiators that trigger polymerization after radiation by UV or visible light are for example benzoinealkyl ether, benzilmonoketals, acylphosphine oxides or aliphatic and aromatic 1,2-diketo-compounds (e.g. camphor chinon).

For accelerating polymerization, so-called activators such as amines or organic phosphites can be added together with the photo-initiators.

The exposure to light of the applied material takes place in the usual equipment-supported manner. It is to be born in mind, though, that the light source has to be compatible with the photo-initiator used, i.e. that the wave length of the emitted light corresponds to the absorption behavior of the photo-initiator. Mixtures of photo-initiators covering a wide absorption range make the process a little more independent of the light source to be used in a particular case.

The initiators are preferably applied in amounts of 0.05 to 3 % by weight relative to the weight of the unsaturated compounds occurring in the compositions.

The cured coatings are resistant against plaque deposits. They are also characterized by homogenous surfaces and do not affect the color of the base material because they are transparent. They are scratch, abrasion and hydrolysis resistant, and offer a good surface hardness.

The coatings as per the invention are suitable for the coating of teeth as well as tooth replacement parts which, in an oral environment, are subject to deposits of dental plaque. The coatings are especially suitable for synthetic materials such as prosthesis base plates, partial prosthesis, artificial teeth, composite fillings, synthetic inlays and, in particular, synthetic facings.

In a special embodiment of the invention, the pre-condensates in terms of the invention can also be mixed with ethylenically unsaturated, co-polymerisable monomers which are homogeneously miscible with the pre-condensate or can be dissolved therein.

Suitable monomers are, for example, (meth)acryl acid and its salts, preferably the alkali metal salts such as sodium salt; (meth)acryl acid ester such as methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, cyclohexyl(meth)acrylate, glycidyl(meth)acrylate, ethyleneglycolmono(meth)acrylate, diethyleneglycolmono(meth)acrylate, triethyleneglycolmono(meth)acrylate, allyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 2-dimethylaminoethyl(meth)acrylate and 3-methoxy-2-hydroxypropyl(meth)acrylate; (meth)acryl acid amides such as (meth)acrylamide, N-methylol(meth)acrylamide, dimethyl(meth)acrylamide; allyl compounds such as allyl alcohol and allylglycidyl ether; N-vinylpyrrolidone and styrol. Especially preferred amongst these monomers are alkyl(meth)acryl acid ester, alkoxyalkyl(meth)acryl acid ester and hydroxyalkyl(meth)acryl acid ester with 1 to 6 carbon atoms in the alkyl and alkoxy groups respectively as well as N-vinylpyrrolidone. The amount of monomers can be 1 to 50 % by weight, preferably 10 to 30 % by weight, relative to the overall weight of pre-condensate and monomers.



The polymerization or co-polymerization can possibly be carried out with one or several unsaturated compounds present as cross-linking agents. Particular examples of suitable cross-linking agents are ethyleneglycoldi(meth)acrylate, diethyleneglycoldi(meth)acrylate, triethyleneglycoldi(meth)acrylate, butyleneglycoldi(meth)acrylate, neopentylglycoldi(meth)acrylate, pentaerythritetri(meth)acrylate, pentaerythritetetra(meth)acrylate, allyl(meth)acrylate, trimethylolpropantri(meth)acrylate, divinylbenzol and diallylphthalate.

Suitable are also the long-chained monomers as per US patent 3,066,112 on the basis of bisphenol-A and glycidylmeth-acrylate or its derivatives formed by the addition of isocyanates. Suitable are also compounds of the type bisphenol-A-diethyl(meth)acrylate and bisphenol-A-dipropyl(meth)acrylate. In addition, the derivatives, mentioned above, of the bisphenol-A types extended with alkoxide units are suitable, such as diacryl or dimethacryl acid esters of bishydroxypolyalkoxy-bisphenol-A derivatives for example.

Suitable in addition to the above are also the diacryl or dimethacryl acid esters of bishydroxymethyltricyclo[5.2.1.0<sup>2,6</sup>]-decans and the derivatives of bishydroxymethyltricyclo[5.2.1.0<sup>2,6</sup>]-decans extended with alkoxide, as mentioned in the German patent 2,816,823. The reaction products from diisocyanates and hydroxyalkyl(meth)acrylates can also be used, as described in the German patent application 23,12,559.

The amount of cross-linking agent is preferably 1 to 50 mol-%, in particular 10 to 30 mol-%, relative to the overall mol quantity of monomers.

Dependent on the selection of the curing conditions, initiators of the above-mentioned type are added to the monomers in the proportion of materials also mentioned above. The application of the coatings and their curing then takes place in the manner described above.

For a special embodiment of the invention, mono or polyfunctional vinyl ethers and vinyl esters, for example, are suitable as cationically curable resins or cationically polymerisable monomers. Suitable vinyl ethers are trimethylolpropan-trivinyl-ether, ethyleneglycol-divinyl-ether and cyclic vinyl ethers. Especially suitable is triethyleneglycol-divinyl-ether.

Generally well-suited compounds are the vinyl esters and vinyl ethers of polyfunctional alcohols, whereby the use of polyethylene and polypropylenglycos with vinyl ether end groups is particularly preferred.

In addition, cationically polymerisable, heterocyclic compounds such as epoxides are well suited. Here, preference is given to the use of glycidyl ethers of mono or polyvalent alcohols such as the diglycidyl ethers of bisphenol-A. For the set-up of a high reactivity, the diepoxides and polyepoxides of aliphatic compounds are particularly well suited, namely the glycidyl ethers and  $\beta$ -methylglycidyl ethers of cycloaliphatic diols and polyols.

Furthermore, glycidyl esters of carbon acids, in particular of dicarbon and polycarbon acids can be used as glycidyl compounds, for example the glycidyl esters of succinic acid, adipic acid, phthalic acid.

Examples of particularly reactive glycidyl compounds are the diepoxides of vinylcyclohexanes and of dicyclopentadiens as well as 3-(3',4'-epoxycyclohexyl)-8,9-

epoxy-2,4-dioxy-spiro-(5,5)undecan and 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexylcarboxylate.

Preferred epoxide resins are possibly pre-extended and/or pre-polymerized diglycidyl ethers of bivalent phenols or bivalent aliphatic alcohols with two to four C atoms. Especially preferred is the use of pre-extended diglycidyl ethers of 2,2-bis-(4-hydroxyphenyl)-propane.

## MANUFACTURING EXAMPLES

### Example 1

13.68g of tetraethoxy-titanate are dissolved in a 50mL mixture of toluol and ethanol (1:1) and 0.6mL of glacial acetic acid are added. This mixture is stirred for 0.5h at 50°C. Separately from this, 30.28g of diphenylsilandiol are dissolved in a mixture of toluol and ethanol (1:1). At a temperature of 50°C and while constantly stirring it, this solution is slowly let drip into the tetraethoxy-titanate solution and subsequently heated to 75°C for 1h under reflux conditions. The solution is cooled down to room temperature, a mixture of 10mL of water and 10mL of ethanol is added in droplets while being stirred and stirring continues for 1h at room temperature. At a reduced pressure, solvent and water are removed at 60°C. The result is a yellowish, transparent, viscous pre-condensate.

### Example 2

13.8g of diphenyldichlor-silane are dissolved in 17.1mL of ethanol, 6.8g of methylvinylchlor-silane in 8.4mL of ethanol and 0.53g of tetraethoxy-titanate in 1.5mL of ethanol. These ethanolic solutions are combined and heated for 2h at 78°C

under reflux conditions. Then, 7.2mL 0.01n[?] of hydrochloric acid are added slowly in droplets at 70°C, and this preparation is kept at this temperature for 0.5h. The solvent and water are removed under a slight vacuum. The remaining silane is dissolved in acetic acid to a 10% solution and 0.2g of dibenzoyl peroxide are added. The coatings were dried at temperatures between 60 and 120°C.

### Example 3

13.1g of diphenyldichlor-silane are dissolved in 15.8mL of ethanol, 6.5g of methylvinylchlor-silane in 7.9mL of ethanol and 1.53g of tetraethoxy silane in 3.0mL of ethanol. These solutions are combined and heated for 2h at 78°C under reflux conditions. Then, 7.2mL 0.01n[?] of hydrochloric acid are added slowly in droplets at 70°C, and this preparation is kept at this temperature for 0.5h. The solvent and water are distilled out under a slight vacuum. The silane is dissolved in acetic acid to a 10% solution and 0.2g of dibenzoyl peroxide are added. The coatings were dried at temperatures between 60 and 120°C.

### Example 4

10.4g of methacryloxypropyltrimethoxy silane and 3.8g methyltrimethoxy silane are mixed at room temperature and 5.75g of butylate-secondary-butylate are added in droplets while being stirred. This mixture is stirred for 10 min. and cooled down to 15°C. Then, 0.84mL of water are slowly added in droplets, stirred for 10 min. and the solution is cooled down to 10°C. Subsequently, 1.68mL of water are slowly added in droplets and, after 15 min. of stirring, a further 5mL of water are added. This product is stirred for 2h. The result is a clear solution from which the solvent is distilled off under a slight vacuum. The remaining product is dissolved in 50mL of acetic ester and the

ester is distilled off in several stages. Finally, a solution of this silane in 50mL of acetic ester is used for coatings. The coatings were dried at 90°C.

#### Example 5

20g of tetraethoxy silane are dissolved in 50mL of ethanol (1:1) and 0.6mL of glacial acetic acid are added. This mixture is stirred for 30 min. at 50°C and a solution of 26.2g diphenylsilanediol is added in a mixture of toluol and ethanol (1:1). At 50°C and while constantly stirring it, this solution is let drip into the tetraethoxy silane solution and subsequently heated to 75°C for 1h under reflux conditions. The solution is cooled down to room temperature, a mixture of 10mL of water and 10mL of ethanol is added while being stirred and stirring continues for 1h at room temperature. At a reduced pressure, solvent and water are removed at 60°C. The result is a colorless, transparent, viscous polymer that can be used for coating purposes.

### APPLICATION EXAMPLES - EXAMINING DEPOSITS OF PLAQUE

#### Example 6

3.5g of the pre-condensate from Example 1 are dissolved in 6.5g of toluol. With a brush, a thin coating is applied to the collocryl-B test piece and dried for 24h at 95°C. The result is a crystal clear, firmly adhering coating.

#### Example 7

The solution prepared in Example 2 is brushed onto the test piece and cured for 12h at 80°C.

Example 8

The solution prepared in Example 4 is mixed with 0.1g of camphor chinon as well as 0.2g of 2-dimethylaminoethylmethacrylate. After applying the coating to the test piece, it is dried for 10 min. at 40°C. With a commercially available cold light unit (EliparII, by ESPE), the coating is cured by exposing it for 40 seconds.

Measuring Principle:

Coated synthetic test pieces were worn by patients for 3 days. Subsequently, the plaque accumulation relative to the coating process was determined by weighing the test pieces.

Material:

PMMA (test piece made of synthetic prosthesis material callocryl-B)

Test piece dimensions: 5 x 7 x 1 mm

Method:

The test pieces were coated in accordance with the invention, dried in a desiccator for obtaining a constant weight and weighed on precision scales. Subsequently, the test pieces were fitted to a carrier in the upper jaw of three subjects (1 female, 2 male, average age 21 years) and worn for 3 days. The carriers were not specially cleaned, just roughly rinsed with water after meals. After the test period, the test pieces were taken off the carrier, dried for 24 hours in the desiccator and weighed again. Table 1 shows the plaque accumulation relative to the coating process in  $\mu\text{g}/\text{cm}^2$ .

Comparative example V1: Test piece not coated

Comparative example V2: Test piece coated with conventional prosthesis lacquer based on acrylate (Palaseal, by Kulzer).

Results: Plaque Accumulation [ $\mu\text{g}/\text{cm}^2$ ]

Subject	V1	V2	Example 6	Example 7	Example 8
<b>I</b>	1.94	1.74	0.47	0.68	0.42
<b>II</b>	1.87	1.68	0.31	0.55	0.38
<b>III</b>	1.98	1.81	0.53	0.48	0.78
<b>Average Values</b>	1.93	1.74	0.44	0.57	0.54

The examples based on the invention show a strongly reduced plaque accumulation when compared to the uncoated test piece (V1).

By contrast, a conventional surface sealing based on an acrylate lacquer does not show a significant reduction of plaque accumulation when compared with uncoated test pieces. Furthermore, the interesting fact emerged that the minor plaque deposits on the test pieces coated in accordance with the invention could be removed very easily while deposits adhered firmly to the comparative test pieces.

In practical terms, this effect is of particular importance because, contrary to current technology, these minor deposits accumulated on coatings as per the invention could be removed easily with a tooth brush.



# THE CLAIMS

## 1. Use of compositions comprising

- (a) at least one compound, soluble in the reaction medium, of formula (I)



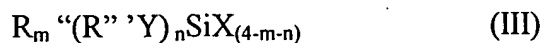
wherein M stands for Ti, Zr, Si, Ge, Sn or Al, R stands for halogen, hydroxy, alkoxy, acyloxy or a chelate ligand and x is the valency of M, as well as

- (b) an organic silane of formula (II)



wherein R'' stands for alkyl, alkenyl, aryl, arylalkyl, alkylaryl, aryl alkenyl, alkenyl aryl, which residues can be interrupted by oxygen atoms or sulphur atoms or –NH groups, X stands for hydrogen, halogen, hydroxy, alkoxy, acyloxy or the group –NR<sub>2</sub>' (R' = hydrogen and/or alkyl) and n has the valency 1, 2 or 3, and/or

- (c) an organofunctional silane of formula (III)



wherein R'', X and n have the above meanings, R'' ' stands for alkylene, phenylene, alkylene phenylene, or alkenylene, which residues can be interrupted by oxygen atoms or sulphur atoms or –NH groups, Y stands for halogen atoms, hydroxy, mercapto, polyol, e.g. glycol or glyceryl, possibly substituted amino, quaternary ammonium, amide, polyamide, aldehyde, keto,

carboxy, carboxylic acid alkyl ester, sulphonic acid, phosphoric acid, epoxy, acryloxy or methacryloxy groups and m has the valency 1,2 or 3 for the manufacture of coatings for teeth and tooth replacement parts.

2. The use as per Claim 1 characterized in that the compositions comprise 1 to 99, preferably 20 to 90, in particular 40 to 80 mol-% of component (a) and correspondingly 1 to 99, preferably 10 to 80, in particular 40 to 60 mol-% of component (b) or the compositions comprise 1 to 99, preferably 20 to 90, in particular 40 to 60 mol-% of component (a) and correspondingly 1 to 99, preferably 10 to 80 and in particular 20 to 60 mol-% of component (c) or the compositions comprise 1 to 98, preferably 20 to 80, in particular 40 to 60 mol-% of component (a), 1 to 98, preferably 10 to 75 and in particular 15 to 50 mol-% of component (b), and 1 to 40, preferably 5 to 30 and in particular 10 to 25 mol-% of component (c).
3. The use as per Claim 1 characterized in that the compositions additionally comprise (d) a low-volatile oxide, soluble in the reaction medium, of an element of the main groups Ia to Va or the secondary groups IVb or Vb of the periodic system, with the exception of titan, zircon, silicon, germanium, tin and aluminum, or, under the reaction conditions, a low-volatile oxide forming compound of one of these elements, soluble in the reaction medium.
4. The use as per Claim 3 characterized in that the compositions comprise 0.1 to 50, preferably 0.5 to 30 and in particular 2 to 20 % by weight of component (d), relative to the overall weight of the basic components (a) to (d).

5. The use as per Claims 1 to 4 characterized in that the basic components (a), (b) and/or (c) and possibly (d) are pre-condensed in the desired material proportions, possibly with the use of suitable catalysts, the pre-condensate is then isolated and dissolved in an organic solvent for the manufacture of coating solutions of a viscosity of about 5 to 80 MPa\*s.
6. The use as per Claim 5 characterized in that the coatings are mixed with an ethylenically unsaturated, co-polymerisable monomer, which is homogeneously miscible with the pre-condensate solution or soluble therein, and a suitable initiator.
7. The use as per Claim 5 characterized in that the amount of ethylenically unsaturated monomers/cross-linking agents are 1 to 50, preferably 10 to 30 % by weight, relative to the overall weight comprising the pre-condensate and the ethylenically unsaturated monomers/cross-linking agents, and the amount of initiator is 0.05 to 3 % by weight, relative to the weight of the ethylenically unsaturated monomers/cross-linking agents.
8. Use of the coating solutions obtained as per Claims 5 to 7 for the manufacture of coatings for teeth and tooth replacement parts characterized in that the coating solutions are applied to the teeth or tooth replacement parts and subsequently cured at temperatures ranging from room temperature to 120°C, and if necessary by radiation with visible light or UV light.

9. Use as per Claim 8 characterized in that the coating solutions are applied to tooth replacement parts made of synthetics.
10. Use as per Claim 9 characterized in that the coating solutions are applied to synthetic facings.

## International Search Report

*[In English]*

Annex to International Search Report

*[In English]*

## International Search Report

*[Translated into English on p. 27]*

International Search Report [continued]

*[Translated into English on p. 27]*



Annex to International Search Report

*[Translated into English on p. 28]*

THIS PAGE BLANK (10/20)